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Cathodic materials for nickel-metal hydride batteries

Caiyun Wang

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**CATHODIC MATERIALS FOR NICKEL-METAL
HYDRIDE BATTERIES**

A thesis submitted in fulfillment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

CAIYUN WANG, B. Sc., M. Sc.

Institute for Superconducting & Electronic Materials

Faculty of Engineering

December 2003

DECLARATION

This is to certify that the work presented in this thesis is original and was carried out by the candidate at the Faculty of Engineering, the University of Wollongong, New South Wales, Australia, and has not been submitted for a degree to any other university or institution.

Caiyun Wang

ABSTRACT

The properties of nickel hydroxide, in particular α -phase nickel hydroxide and spherical nickel hydroxide, were studied. α -phase nickel hydroxide was prepared by an improved chemical co-precipitation method, while a spray drying technique was employed to obtain spherical shaped particles. The possible use of this new type of solid polymer electrolyte in Ni/MH batteries was also investigated in this work.

The element Al was chosen to stabilize the structure of α -phase nickel hydroxide, that is turbostratic disorder. The content of Al in Al-substituted nickel hydroxide, $\text{Ni}_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3)_{x/2} \cdot n\text{H}_2\text{O}$, was $x = 0.10, 0.20, 0.25$ and 0.33 . The as-prepared nickel hydroxide sample was aged in 6M KOH for 90 days, and the structure was identified by XRD and TEM techniques. Cyclic Voltammetry, the Tafel Curve and discharge behaviors were employed to investigate the electrochemical properties, and the redox potentials, exchange current density, discharge capacity and voltage are discussed. The Al-substituted nickel hydroxide samples show superior electrochemical performance to β -nickel hydroxide.

A new type of α -phase nickel hydroxide was also prepared and investigated in this study, (Al,Co)-substituted nickel hydroxide. Co together with Al was doped to nickel hydroxide, $\text{Ni}_{1-x}(\text{Al}+\text{Co})_x(\text{OH})_2(\text{CO}_3)_{x/2} \cdot n\text{H}_2\text{O}$, and the content of (Al+Co) was $x = 0.25$. It was found that Al and Co had entered the structure of nickel hydroxide. A higher capacity but lower discharge voltage was obtained compared with Al-Ni(OH)₂ with 25% Al.

The temperature effect on three types of nickel hydroxides, Al–Ni(OH)₂ with 25% Al, (Al,Co)–Ni(OH)₂ ((Al+Co) = 0.25, Co/Al = 0.5) and β-nickel hydroxide, was investigated. The temperatures investigated were –15°C, 0°C, 25°C and 50°C. The samples' charge/discharge behavior and cycle life were investigated. It was found that Al–Ni(OH)₂ and (Al,Co)–Ni(OH)₂ possess the optimum electrochemical performance at 0°C, while β-nickel hydroxide shows its best at 25°C. The samples showed different resistance to the temperature effect, while the highest endurance to low temperature occurred with Al–Ni(OH)₂ and to high temperature with (Al,Co)–Ni(OH)₂.

Spherical agglomerates of nanostructured beta-type Ni(OH)₂ were produced by a spray drying technique. This material features a narrow Gaussian-type particle size distribution in the range of 0.1 – 10 microns and a high specific surface area of 50 – 200 m²/g. The spray drying technique was also tried for preparing spherical Al–substituted nickel hydroxide, and the results show that spherical agglomerates could not be obtained under the same conditions as for β-type. Certain parameters needed to be changed, the air temperature, the spray speed and the ageing period of the nickel hydroxide slurry, and spherical agglomerate particles of Al–Ni(OH)₂ was obtained.

A new type of solid polymer electrolytes, tetramethylammonium hydroxide pentahydrate (TMAH5)–based with addition of poly(tetramethyl ammonium acrylate) (PTMA) were investigated with a view to its possible use as an electrolyte in Ni/MH batteries. The contents of PTMA in the electrolytes were 0%, 5% and 15%. It was found that the Ni/MH cells employing such solid electrolytes were dischargeable, and

the electrochemical performance of TMAH5 + 5% PTMA and TMAH5 + 15% PTMA was improved at 50°C compared with that at 25°C.

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